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"Crystal Growth in Substrate-Confined Liquids"

FINAL TECHNICAL REPORT

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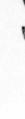
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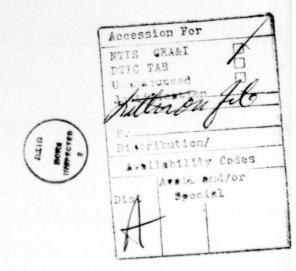
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SUMMARY

The task objective was development of crystal growth techniques utilizing substrate-confined liquids, with emphasis on crystals for photodection. Various techniques were developed, which were successful in growing arrays of metallic crystals such as In and Sb on inert (i.e. non-epitaxial) substrates. These techniques have not yet been successful, however, in growing crystals of the emphasized semiconducting materials, such as InSb or CdTe.

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DETAILED REPORT

A variety of experimental techniques were employed to grow arrays of crystals of such materials as In, Sn, Sb, Ge and, with less success, InSb. Principle substrates used were amorphous SiO₂ and graphite. Many of these techniques were discussed in individual detail in earlier Technical Reports. The discussion in this Final Report, however, is organized around some common features of all the techniques. In this way some indication may be provided of the factors allowing successful growth of some materials, particularly elemental ones, and not others, particularly compounds.

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1. Purity of the Material Deposited at Each Location of the Array.

Many experimental indications were present in the course of these experiments pointing to variable degrees of purity. Electron microprobe analyses were made from time to time and occasionally detected gross impurities in the 10 to 100 ppm range. More commonly, however, deposits were clean by microprobe standards, but showed variability in their wetting behavior. For example, indium deposits on a flat substrate would often melt in dry H_2 into elongated or elliptical shapes as seen in a top (optical) view. On treatment in wet H₂, the indium droplets would assume the circular shape expected in the absence of impurities. Correspondingly, the crystals grown under the latter conditions had a uniform basal orientation to the substrate surface and exhibited facets, most prominently on their uppermost surfaces. On the other hand, the former growth conditions resulted in little if any evidence of oriented crystallization. Thus we were often in the position that the principal checks for purity, spectrographic analysis and microprobe, revealed no impurities, yet other, non-quantitative indications suggested a role for impurities. These latter indications were consistent with the hypothesis that carbonaceous impurities were involved. If this hypothesis is correct, materials such as In or Sn which can be cleaned in wet ${\rm H_2}$ are more suited to these non-epitaxial array growth techniques than are elements that are more easily oxidized, e.g. Ga (borderline) or Al.

2. Confinement of Liquid Droplets to Proper Coordinate Locations in the Array.

A considerable effort was devoted to preparing and using substrates containing arrays of concavities or pits. These pits serve to retain droplets on (or in) the substrate surface and were also anticipated to assist in orienting crystal growth. Two current theories bear on this point: "diataxy", proposed and investigated in Soviet-related countries and "grapho-epitaxy", similarly develoed at Lincoln Labs. However, the orientation expected by either theory was never observed in our experiments. Instead a basal orientation only, i.e. with no associated azimuthal orientation, was observed in our work, and most completely studied in the case of In deposits.

Given the above result, the advantages of pits in the substrate are considerably diminished. Thus further investigations, such as those we are continuing on a limited scale after the completion of this contract, can in most cases utilize flat substrates, with a consequent simplification of the experiments.

For the record, however, it is worth pointing out that considerable knowledge of the stability of droplets in pits was gained in the course of this contract. Pits stabilize droplets at desired locations, result in much flatter meniscus shapes than occur on flat substrates, and may have other uses in various specific applications, particularly in regard to electrical contacting. They could easily be reinvolved should further work with flat substrates prove interesting.

3. Crystal Location: Substrate Interface Versus Within Fluid Phases.

A very different situation results whether a crystal nucleates within fluid phases (i.e. within the liquid or at the liquid-gas interface) or nucleates at the liquid-substrate interface. (Here we are implicitly assuming that the nucleated crystal remains and grows at the original nucleation site). We have observed both cases:

- (a) When Ge was grown from Au-Ge hypereutectic alloy, nucleation occurred within the fluid phases in every case studied. This is perhaps not surprising, since Au-Ge liquids wet Ge very well (e.g. with contact angle \sim 15°) and Ge itself develops, when liquid, a very large contact angle, \sim 155°, against the SiO₂ substates we used.
- (b) Crystallization of In on SiO₂ substrates, by contrast, appears to occur at the liquid-substrate interface. A basal orientation develops at the substrate interface, through the reentrant angles and contours produced in our substrates did not yield azimuthal orientation.

These results have several implications for future studies and for possible applications. Cases like (a), i.e. where nucleation occurs within fluid phases, would only be interesting where an array of crystals with random orientations would be useful. Such is not often the case since any further processing would be difficult, e.g. etching or epitaxial growth. Furthermore, adherence of the crystals to the substrate is a serious problem: if surrounding material (e.g. Au-Ge eutectic in the example above) is removed, adherence to the substrate is lost. On the other hand, partial removal of surrounding material in any uniform way in an array is difficult, given the random

orientation of the crystals of the array.

On the other hand, cases like (b) may still be quite useful, although azimuthal orientation is lacking. Adherence is good, since crystal attaches itself to substrate in the first place. Etching to remove any second phase present can still be accomplished. And the basally oriented array of crystals is suited to further processing, e.g. epitaxial growth. The major difficulty, however, is that the list of materials that grow easily this way does not yet include those of interest for detectors, e.g. CdTe.

Papers published with DARPA support during this contract:

- T. F. Kuech and J. O. McCaldin, "Behavior of Substrate-Confined Liquids for In Situ Crystallization of Semiconductors", Thin Solid Films, 97, 9-16 (1982).
- Masaaki Ueda, J. O. McCaldin, and Rindge Shima, "Crystallization of Substrate-Confined Liquid Indium", Thin Solid Films, 98, 241-247 (1982).
- T. F. Kuech and J. O. McCaldin, "HgTe/CdTe Heterojunctions: A
 Lattice-Matched Schottky Barrier Structure", J. Appl. Phys. <u>53</u>(4),
 3121 3128 (1982).